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(54) 【発明の名称】 リチウム二次電池正極用リチウムマンガン酸化物

(57) 【要約】

【目的】スピネル構造の  $\text{Li}_x\text{Mn}_2\text{O}_4$  を正極活物質とするリチウム二次電池の放電容量の大幅な増大を可能とするリチウム二次電池用スピネル構造  $\text{Li}_x\text{Mn}_2\text{O}_4$  の製造方法を提供することを目的とするものである。

【構成】  $10\mu\text{m}$  以下の電解二酸化マンガンと炭酸リチウムをリチウムとマンガンのモル比  $0.51-0.53$  で混合し、 $600-650^\circ\text{C}$  で焼成して酸素リッチのスピネル化合物とした後、最終的に  $700-750^\circ\text{C}$  で焼成することを特徴とするリチウム二次電池用スピネル構造  $\text{Li}_x\text{Mn}_2\text{O}_4$  の製造方法。

【0001】

【特許請求の範囲】

1. 粒径 $10\mu\text{m}$ 以下の二酸化マンガンを炭酸リチウムを $600-650^\circ\text{C}$ で焼成し、再び $700-800^\circ\text{C}$ で焼成する $\text{Li}/\text{Mn}$ 原子比 $0.51-0.53$ のスピンル化合物の製造方法。

2. 前述のスピンル化合物を正極活物質とするリチウム二次電池用正極。

【0002】

【発明の詳細な説明】

【産業上の利用分野】本発明は、金属リチウムあるいはリチウム-グラファイト（リチウム-カーボン）などのインターカレーション化合物を負極活物質とするリチウム二次電池において、正極活物質に用いられるスピンル構造の $\text{Li}_x\text{Mn}_2\text{O}_4$ の製造方法に関する。

【0003】

【従来の技術および問題点】スピンル構造の $\text{Li}_x\text{Mn}_2\text{O}_4$ の主な製造方法としては炭酸リチウムと $\text{Mn}_2\text{O}_3$ あるいは $\text{Mn}_3\text{O}_4$ とを所定のモル比なるよう混合した後、 $600-650^\circ\text{C}$ で加熱処理してリチウム塩を分解させ、更に $800-900^\circ\text{C}$ で加熱処理する方法（Hunter, J. Solid State Chem., 39, 142 (1981)）が一般的である。

【0004】しかしながら、このようにして得られるスピンル構造の $\text{Li}_x\text{Mn}_2\text{O}_4$ を正極活物質として用いた場合、得られるリチウム二次電池の放電容量が小さく、且つサイクル特性も悪いという問題があった。Manevらは（J. Power Sources, 41, 305 (1993)） $\text{Mn}_2\text{O}_3$ を原料とし $600^\circ\text{C}$ 以上で焼成すると焼結が進み比表面積の小さいスピンル化合物が生成するため得られた $\text{Li}_x\text{Mn}_2\text{O}_4$ のリチウム電池特性が悪くなることを示し、原料としては電解二酸化マンガンをあるいは化学合成二酸化マンガンを適することを明らかにしている。現在高性能の $\text{Li}_x\text{Mn}_2\text{O}_4$ を製造する方法を挙げると次の二つになる。一つはTarasconら（J. Electrochem. Soc., 139, 937 (1992)）による合成法で、この方法ではマンガンを原料を電解二酸化マンガんとしリチウム塩に炭酸リチウムあるいはリチウムを用い、 $800^\circ\text{C}$ での焼成、徐冷、粉碎というプロセスを3回繰り返し、電池特性の優れたスピンル構造の $\text{Li}_x\text{Mn}_2\text{O}_4$ を製造している。しかし、この方法は製造に長時間を要するのみならず製造コストも高くなる難点を有する。もう一つは芳尾ら（J. Power Sources, 54, 483 (1995)）による溶融含浸法と呼ばれる合成法である。この合成法ではリチウム塩に硝酸リチウムや水酸化リチウムを用い、電池特性の優れたスピンル構造の $\text{Li}_x\text{Mn}_2\text{O}_4$ を1回の焼成プロセスで製造できる。しかしながら、硝酸リチウムは吸湿性が強く、リチウムとマンガンを所定のモル比に保つことは困難であ

るばかりでなく、焼成時発生する環境汚染物質の $\text{NO}_x$ を発生する問題点も有する。水酸化リチウムも空気中の炭酸ガスを吸収して炭酸リチウムを生成するため、原料の保存、管理に細心の注意が必要であり、工業的な生産には不向きである。

【0005】

【発明が解決しようとする課題】本発明は、かかる従来技術の有する課題に鑑みてなされたものであり、スピンル構造の $\text{Li}_x\text{Mn}_2\text{O}_4$ を正極活物質とするリチウム二次電池の放電容量の大幅な増大を可能とするリチウム二次電池用スピンル構造 $\text{Li}_x\text{Mn}_2\text{O}_4$ の製造方法を提供することを目的とするものである。

【0006】

【問題を解決するための手段】本発明は、かかる従来技術の課題に鑑みなされたもので、原料電解二酸化マンガンの粒径を $10\mu\text{m}$ 以下とし、リチウムとマンガンのモル比を $0.51-0.53$ とし、炭酸リチウムの溶融分解温度で焼成した後、冷却後粉碎してさらに高温の $700-750^\circ\text{C}$ で焼成することにより達成された。

【0007】すなわち、本発明はマンガンを原料に焼結の進みにくい二酸化マンガンを選択し、粒径を小さくすることにより焼結が進んでも表面積の低下を抑制することを目指したものである。二酸化マンガ粒子の粒径が $10\mu\text{m}$ 以下としているため通常のアルカリ電池用電解二酸化マンガ（平均粒径約 $40\mu\text{m}$ ）を用いた場合よりも炭酸リチウムと二酸化マンガンの混合時の均一分布性が著しく増加する。この為局所的な $\text{Li}/\text{Mn}$ 比の違いがなくなり電気化学的に不活性な $\text{Mn}_2\text{O}_3$ や $\text{Li}_2\text{MnO}_3$ の生成が防止できる。粒径の大きな電解二酸化マンガを用いると局所的な $\text{Li}/\text{Mn}$ 比の違いが生じ $\text{Hn}_2\text{O}_3$ や $\text{Li}_2\text{MnO}_3$ が生成するため、Tarasconらのように粉碎混合、再焼成というプロセスを経なければ電池特性の優れたスピンル構造 $\text{Li}_x\text{Mn}_2\text{O}_4$ は合成できない。炭酸リチウムと二酸化マンガは $400^\circ\text{C}$ で反応し、酸素リッチなスピンル化合物が生成するばかりでなく、合成にも長時間を要する。合成温度を炭酸リチウムの溶融温度以上にする（ $600-650^\circ\text{C}$ ）と炭酸リチウムが液体状となって表面を覆うため $\text{Li}$ と $\text{Mn}$ の分布の均一性は混合時よりも更に向上することになる。反応も固液反応となり、スピンル化合物も10時間以内で生成し、操作性も向上する。この時点で生成するスピンル化合物はX線回折（XRD）的には単一相であり、立方晶系格子定数が $8.2\text{\AA}$ 以下の酸素リッチな放電容量の小さい化合物である。XRD的には不純物相の生成は認められないが、 $\text{Mn}_2\text{O}_3$ や $\text{Li}_2\text{MnO}_3$ 相の消失をより確実なものとするため粉碎を行った後、 $700-750^\circ\text{C}$ で焼成して目的とするスピンル構造の $\text{Li}_x\text{Mn}_2\text{O}_4$ を合成した。

【0008】

【作用】本発明により得られたスピンル構造 $\text{Li}_x\text{Mn}$

2 O<sub>4</sub> 従来の炭酸リチウムを用いる方法で合成したスピネル構造Li<sub>x</sub>Mn<sub>2</sub>O<sub>4</sub>よりも顕著な効果を奏するのは、原料マンガ酸化物の粒径が小さいため、炭酸リチウムとマンガ酸化物の分布が均一になること、および炭酸リチウムの溶融温度まで温度をあげることで炭酸リチウムが溶融してマンガ酸化物と反応するのでマンガ酸化物とリチウムの反応が速やかに且つ均一に進行するためである。この為、本発明の合成法では不純物のMn<sub>2</sub>O<sub>3</sub>やLi<sub>2</sub>MnO<sub>3</sub>が生成することがない。このことがリチウム二次電池正極活物質として用いた場合に放電容量が大きくなる原因である。

【0009】

【実施例】以下、実施例等に基づいて本発明を具体的に説明する。

【実施例1】電解二酸化マンガ20gと炭酸リチウム4.2434g(Li/Mn比:0.524)を粉碎混合し、アルミナ容器に入れる。この試料容器を電気炉にいれ、室温から600℃まで6時間で昇温し、600℃で10時間保持した。1時間で室温まで冷却し、試料を取り出した。この試料のXRD図にはMn<sub>2</sub>O<sub>3</sub>やLi<sub>2</sub>MnO<sub>3</sub>のピークは存在せず、Li<sub>x</sub>Mn<sub>2</sub>O<sub>4</sub>のみの回折ピークが認められた。回折ピークより格子定数を計算すると8.19Åであり、酸素リッチのスピネル化合物が生成している。酸素含量を減少させるためこの試料を750℃で24時間焼成すると格子定数の値は8.22Åまで増加した。この試料を正極活物質として以下に示すリチウム二次電池を構成した。なお、リチウム二次電池には内径18mmの充放電用電池を用い、構成作業はアルゴンは雰囲気下のドライボックス中で行った。図1中、1は負極端子、2は絶縁物、3は負極集電板、4は金属リチウム、5はセパレーター、6はガラスフィルター用紙、7は正極合剤、8は正極端子を示す。正極合剤としては得られたLi<sub>x</sub>Mn<sub>2</sub>O<sub>4</sub>の25mgに導電性バインダー10mgを加え、フィルム状とした後18φmmとしてステンレス製集電板に圧着した。電解液としては炭酸エチレンと炭酸ジメチルの1:2混合溶媒にLiPF<sub>6</sub>(1mole/l)を溶解したものをを用いて1mAの電流で4.5-3.5Vの範囲の電圧で充放電を繰り返した。図2にこの電池のサイクル特性を示す。1サイクル目の放電容量は129mAh/gであり、50サイクル目でも122mAh/gの放電容量を示す。

【比較例1】マンガ原料に平均粒径約40μmの電解二酸化マンガを用い、実施例1と同じ条件で合成を行った。最終生成物のXRD測定を行うと(311)面のピークより低角側にMn<sub>2</sub>O<sub>3</sub>のピークが認められる。この試料の1回目の放電容量は90mAh/gにすぎず、実施例と比べ40mAh/gも低い。この試料を粉碎と750℃で24時間の再焼成を2回施すとXRD図

からMn<sub>2</sub>O<sub>3</sub>のピークが消失した。また、放電容量も120mAh/gまで増加した。

【比較例2】リチウムとマンガンのモル比を0.50あるいは0.54として実施例1の方法に従い、Li<sub>x</sub>Mn<sub>2</sub>O<sub>4</sub>の合成を行った。モル比0.50ではMn<sub>2</sub>O<sub>3</sub>が副生し、一方モル比0.54ではLi<sub>2</sub>MnO<sub>3</sub>が副生することがXRDから確認できた。モル比0.50でMn<sub>2</sub>O<sub>3</sub>が副生するのは原料電解二酸化マンガが硫酸根を1wt%含むためであろう。モル比0.51および0.53では単一相のLi<sub>x</sub>Mn<sub>2</sub>O<sub>4</sub>が生成することから本合成法が適用できるのはリチウムとマンガンのモル比が0.51-0.53の範囲である。

【0010】

【実施例2】電解二酸化マンガ20gと炭酸リチウム4.2434g(Li/Mn比:0.524)を粉碎混合し、アルミナ容器に入れる。この試料容器を電気炉にいれ、室温から600℃まで6時間で昇温し、600℃で10時間保持した。さらに1時間で750℃まで昇温し、750℃で24時間焼成した。生成物は単一相のLi<sub>x</sub>Mn<sub>2</sub>O<sub>4</sub>であり格子定数は8.22Åと実施例1と同じ値であった。図3に充放電曲線を示す。放電曲線の形状は実施例1の試料と同じであり、1サイクル目の放電容量は124mAh/gで実施例1よりもわずかに小さくなった。

【0011】

【発明の効果】以上説明したように10μm以下の電解二酸化マンガと炭酸リチウムを600-650℃で焼成し、酸素リッチのスピネル化合物とした後、最終的に700-750℃で焼成することにより放電容量が大きく、サイクル特性の優れたLi<sub>x</sub>Mn<sub>2</sub>O<sub>4</sub>が得られる。

【図面の簡単な説明】

【図1】本発明に係わるリチウム二次電池の構造を示す断面図である。

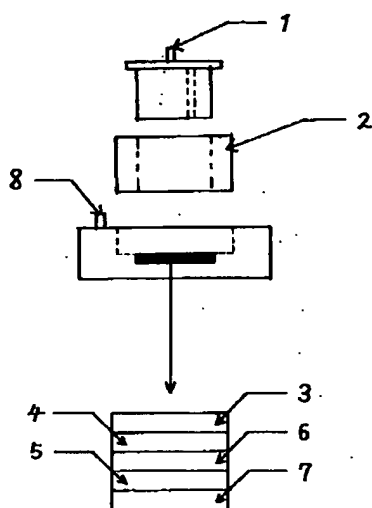
【図2】本発明により得られたLi<sub>x</sub>Mn<sub>2</sub>O<sub>4</sub>のサイクル数と放電容量の関係を示す図である。

【図3】実施例2より得られたLi<sub>x</sub>Mn<sub>2</sub>O<sub>4</sub>の充電および放電曲線である。

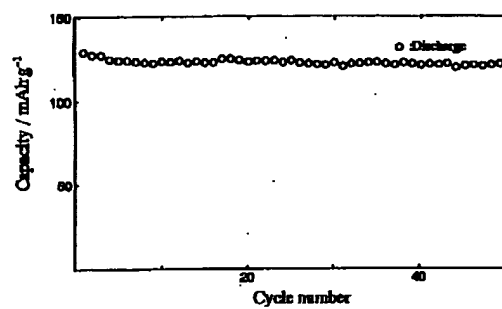
【符号の説明】

- 1 負極端子
- 2 絶縁物
- 3 負極集電板
- 4 金属リチウム
- 5 セパレーター
- 6 ガラスフィルター用紙
- 7 正極合剤
- 8 正極端子
- 9 充電曲線
- 10 放電曲線

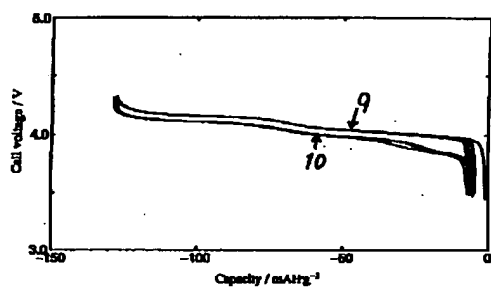
【図1】



【図2】



【図3】



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### (54) LITHIUM MAGNESIUM OXIDE FOR ANODE OF LITHIUM SECONDARY BATTERY

(57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain a spinel structure  $\text{Li}_x\text{Mn}_2\text{O}_4$  compound specified in a Li/Mn atomic ratio, used for secondary battery, and enabling a large increase in the discharge capacity of the lithium battery using the spinel structure  $\text{Li}_x\text{Mn}_2\text{O}_4$  as an active anode substance by twice calcining manganese dioxide and lithium carbonate having specific particle diameters, respectively.

**SOLUTION:** Electrolytic magnesium dioxide and lithium carbonate having particle diameters, respectively, are calcined in a lithium/manganese molar ratio of 0.51-0.53 at a temperature (600-650° C) above the melting decomposition temperature of the lithium carbonate, cooled, ground and again calcined at a high temperature of 700-750° C to obtain the spinel structure  $\text{Li}_2\text{Mn}_2\text{O}_4$  more improved in the homogeneity of Li-Mn distribution than that when the raw materials are mixed. The reaction is a solid-liquid reaction, and the spinel compound is produced within 10hr. The operability is also improved. Although the first produced spinel compound is a compound exhibiting a single phase by an X-ray diffraction method (XRD), having a cubic system lattice constant of  $\leq 8.2\text{\AA}$ , rich in oxygen and small in a discharge capacity, the compound is again calcined for ensuring the elimination of  $\text{Mn}_2\text{O}_3$  and  $\text{Li}_2\text{MnO}_3$  phases to obtain the objective product.

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Industrial Application] this invention relates to the manufacture method of  $\text{Li}_x\text{Mn}_2\text{O}_4$  of Spinel structure used for a positive active material in the lithium secondary battery which makes intercalation compounds, such as metal lithium or lithium-graphite (lithium-carbon), a negative-electrode active material.

[0003]

[Description of the Prior Art] as the main manufacture methods of  $\text{Li}_x\text{Mn}_2\text{O}_4$  of Spinel structure -- a lithium carbonate,  $\text{Mn}_2\text{O}_3$ , or  $\text{Mn}_3\text{O}_4$  -- predetermined -- a mole ratio -- it needs -- after mixing, the method (Hunter, J. Solid State Chem., 39,142 (1981)) of heat-treating at 600 to 650 degree C, and making decompose lithium salt and heat-treating at further 800 to 900 degree C is common

[0004] However, when  $\text{Li}_x\text{Mn}_2\text{O}_4$  of the Spinel structure obtained by doing in this way was used as a positive active material, there was a problem that a cycle property was also bad, small [ the service capacity of the lithium secondary battery obtained ]. The lithium cell property of  $\text{Li}_x\text{Mn}_2\text{O}_4$  obtained in order that sintering might progress and a spinel compound with a small specific surface area might generate, if Manev and others used  $\text{Mn}_2\text{O}_3$  as a raw material and it calcinated above 600 degrees C shows a bird clapper bad, and it is shown clearly that an electrolytic manganese dioxide or chemosynthesis manganese dioxide is suitable as a raw material. It will be set to the following two if the method of manufacturing  $\text{Li}_x\text{Mn}_2\text{O}_4$  of an amount-on-hand performance is mentioned. One is a synthesis method by Tarascon and others (J. Electrochem. Soc., 139,937 (1992)), and by this method, it makes a manganese raw material an electrolytic manganese dioxide, uses a lithium carbonate or a lithium for lithium salt, repeats the process of baking at 800 degrees C, annealing, and trituration 3 times, and is manufacturing  $\text{Li}_x\text{Mn}_2\text{O}_4$  of the Spinel structure which was excellent in the cell property. However, this method has the difficulty manufacture not only takes a long time, but that a manufacturing cost becomes high. Another is a synthesis method called melting sinking-in method by Yoshio and others (J. Power Sources, 54,483 (1995)). At this synthesis method, a lithium nitrate and a lithium hydroxide are used for lithium salt, and  $\text{Li}_x\text{Mn}_2\text{O}_4$  of the Spinel structure which was excellent in the cell property can be manufactured in 1 time of a baking process. However, it also has the trouble of a lithium nitrate being not only difficult for hygroscopicity to be strong and to maintain a lithium and manganese at a predetermined mole ratio, but generating  $\text{NO}_x$  of the quality of an environmental pollutant generated at the time of baking. In order that a lithium hydroxide may also absorb the carbon dioxide gas in air and may generate a lithium carbonate, careful cautions are required for preservation of a raw material and management, and it is unsuitable for industrial production.

[0005]

[Problem(s) to be Solved by the Invention] this invention is made in view of the technical problem which this conventional technology has, and offers the manufacture method of Spinel structure  $\text{Li}_x\text{Mn}_2\text{O}_4$  for lithium secondary batteries which enables large increase of the service capacity of the lithium secondary battery which makes  $\text{Li}_x\text{Mn}_2\text{O}_4$  of Spinel structure a positive active material -- it aims at things

[0006]

[Means for Solving the Problem] this invention was attained by having ground after cooling and calcinating at 700 to 750 further hot degree C, after having been made in view of the technical problem of this conventional technology, having set particle size of a raw material electrolytic manganese dioxide to 10 micrometers or less, setting the mole ratio of a lithium and manganese to 0.51-0.53 and calcinating by the melting decomposition temperature of a lithium carbonate

[0007] That is, it aims at that this invention suppresses the fall of a surface area although sintering progresses by choosing as a manganese raw material manganese dioxide to which sintering cannot progress easily, and making particle size small. Since the particle size of the manganese dioxide particle is setting to 10 micrometers or less, the uniform distribution nature at the time of mixture of a lithium carbonate and manganese dioxide increases from the case where the usual electrolytic manganese

dioxide for alkaline cells (about 40 micrometers of mean particle diameters) is used, remarkably. For this reason, the difference in a local Li/Mn ratio is lost, and inactive Mn 2O<sub>3</sub> and generation of Li<sub>2</sub>MnO<sub>3</sub> can be prevented electrochemically. If it does not pass through the process of trituration mixture and re-baking like Tarascon and others in order that the difference in a local Li/Mn ratio may arise and Mn 2O<sub>3</sub> and Li<sub>2</sub>MnO<sub>3</sub> may generate, if an electrolytic manganese dioxide with a big particle size is used, Spinel structure LixMn 2O<sub>4</sub> which was excellent in the cell property is uncompoundable. a lithium carbonate and manganese dioxide -- 400 degrees C -- reacting -- oxygen -- a rich spinel compound not only generates, but composition takes a long time synthetic temperature -- more than the melting temperature of a lithium carbonate -- carrying out (600 to 650 degree C) -- a lithium carbonate serves as a liquid and, for a wrap reason, the homogeneity of a distribution of Li and Mn will improve a front face further rather than the time of mixture It becomes a solid-liquid reaction, and a reaction also generates a spinel compound within [ in 10 hours ], and its operation nature also improves. the spinel compound generated at this time -- an X diffraction (XRD) ---like -- a single phase -- it is -- a cubic system lattice constant -- oxygen 8.2A or less -- it is the small compound of rich service capacity Although generation of an impurity phase was not accepted in XRD, after grinding in order to make disappearance of Mn 2O<sub>3</sub> or a Li<sub>2</sub>MnO three phase circuit into a more positive thing, LixMn 2O<sub>4</sub> of the Spinel structure which calcinates at 700 to 750 degree C, and is made into the purpose was compounded.

[0008]

[Function] since doing a remarkable effect so has a particle size of a raw material manganic acid ghost smaller than Spinel structure LixMn 2O<sub>4</sub> compounded by the method using the lithium carbonate of the Spinel structure LixMn2O<sub>4</sub> former obtained by this invention, and a lithium carbonate fuses since the distribution of a lithium carbonate and a manganic acid ghost raises temperature to the melting temperature of a bird clapper and a lithium carbonate uniformly and it reacts with a manganic acid ghost, it is for the reaction of a manganic acid ghost and a lithium to advance to homogeneity promptly For this reason, by the synthesis method of this invention, neither Mn 2O<sub>3</sub> of an impurity nor Li<sub>2</sub>MnO<sub>3</sub> generates. When this uses as a lithium secondary battery positive active material, it is the cause by which service capacity becomes large.

[0009]

[Example] Hereafter, based on an example etc., this invention is explained concretely.

[Example 1] Trituration mixture of 20g of electrolytic manganese dioxides and the 4.2434g (Li/Mn ratio : 0.524) of the lithium carbonates is carried out, and it puts into an alumina container. This specimen container was paid to the electric furnace, the temperature up was carried out from a room temperature to 600 degrees C in 6 hours, and it held at 600 degrees C for 10 hours. It cooled to the room temperature in 1 hour, and the sample was taken out. Neither Mn 2O<sub>3</sub> nor the peak of Li<sub>2</sub>MnO<sub>3</sub> existed in the XRD view of this sample, but the diffraction peak of only LixMn 2O<sub>4</sub> was accepted. if a lattice constant is calculated from a diffraction peak -- 8.19A -- it is -- oxygen -- the rich spinel compound is generating In order to decrease an oxygen content, when this sample was calcinated at 750 degrees C for 24 hours, the value of a lattice constant increased to 8.22A. The lithium secondary battery shown below by making this sample into a positive active material was constituted. In addition, the argon performed activity to the lithium secondary battery in the dry box under atmosphere using the cell for charges and discharges with a bore of 18mm. the inside of drawing 1 , and 1 -- a negative-electrode terminal and 2 -- an insulator and 3 -- a negative-electrode collecting electrode plate and 4 -- a metal lithium and 5 -- a separator and 6 -- a glass-filter filter paper and 7 -- a positive electrode -- a mixture and 8 show a positive-electrode terminal a positive electrode -- conductive binder 10mg was added to 25mg of LixMn 2O<sub>4</sub> obtained as a mixture, and after considering as the shape of a film, it was stuck to the collecting electrode plate made from stainless steel by pressure as 18phimm Charge and discharge were repeated on the voltage of the range of 4.5-3.5V by 1mA current using what dissolved LiPF<sub>6</sub> (1 mole/l) in 1:2 mixed solvents of an ethylene carbonate and a dimethyl carbonate as the electrolytic solution. The cycle property of this cell is shown in drawing 2 . The service capacity of 1 cycle eye is 129 mAh/g, and shows the service capacity of 122 mAh/g also by 50 cycle eye.

[The example 1 of comparison] The electrolytic manganese dioxide of about 40 micrometers of mean particle diameters was used for the manganese raw material, and it compounded on the same conditions as an example 1. If XRD measurement of an end product is performed (311), the peak of Mn 2O<sub>3</sub> will be accepted in a low angle side from the peak of a field. For the 1st service capacity of this sample, it does not pass to 90 mAh/g, but compares with an example, and 40 mAh/g is also a low. When re-baking of 24 hours was given twice for this sample at trituration and 750 degrees C, the peak of Mn 2O<sub>3</sub> disappeared from the XRD view. Moreover, service capacity also increased to 120 mAh/g.

[The example 2 of comparison] LixMn 2O<sub>4</sub> was compounded according to the method of an example 1, having used the mole ratio of a lithium and manganese as 0.50 or 0.54. In the mole ratio 0.50, it has checked from XRD that Mn 2O<sub>3</sub> carries out a byproduction, and Li<sub>2</sub>MnO<sub>3</sub> carries out a byproduction by the mole ratio 0.54 on the other hand. Mn 2O<sub>3</sub> carries out a byproduction by the mole ratio 0.50 -- a raw material electrolytic manganese dioxide -- a sulfuric-acid solution -- 1wt% -- it will be because it contains In mole ratios 0.51 and 0.53, since LixMn 2O<sub>4</sub> of a single phase generates, the range of the mole ratio of a lithium and manganese of this synthesis method being applicable is 0.51-0.53.

[0010]

[Example 2] Trituration mixture of 20g of electrolytic manganese dioxides and the 4.2434g (Li/Mn ratio : 0.524) of the lithium carbonates is carried out, and it puts into an alumina container. This specimen container was paid to the electric furnace, the temperature up was carried out from a room temperature to 600 degrees C in 6 hours, and it held at 600 degrees C for 10 hours. The temperature up was carried out to 750 degrees C in 1 more hour, and it calcinated at 750 degrees C for 24 hours. The product was LixMn 2O<sub>4</sub> of a single phase, and the lattice constant was the same value as 8.22A and an example 1. A charge-and-discharge curve is shown in drawing 3. The configuration of a discharge curve is the same as the sample of an example 1, and the service capacity of 1 cycle eye became small slightly rather than the example 1 by 124 mAh/g.

[0011]

[Effect of the Invention] it explained above -- as -- an electrolytic manganese dioxide and a lithium carbonate 10 micrometers or less -- 600 to 650 degree C -- calcinating -- oxygen -- after considering as a rich spinel compound, by finally calcinating at 700 to 750 degree C, service capacity is large and LixMn 2O<sub>4</sub> which was excellent in the cycle property is obtained

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[Translation done.]

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**Lithium-Manganese Oxide for Anode of Lithium Secondary Battery**

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[0001]

[Claims]

1. A method of production of a spinel compound having a Li/Mn atomic ratio of 0.51-0.53, wherein manganese dioxide having a particle size of 10 $\mu$ m or smaller and lithium carbonate are fired at 600-650°C and again fired at 700-800°C.

2. An anode for lithium secondary battery, wherein said spinel compound is used as an active anode substance.

[0002]

[Detailed Explanation of the Invention]

[Field of Use in the Industry] The present invention relates to a method of production of spinel structure  $\text{Li}_x\text{Mn}_2\text{O}_4$  which is used for an active anode substance in a lithium secondary battery having an intercalation compound such as metallic lithium or lithium-graphite (lithium-carbon) as an active cathode substance.

[0003]

[Prior Art and Problems] The main method of production of spinel structure  $\text{Li}_x\text{Mn}_2\text{O}_4$  is generally the method (Hunter, J. Solid State Chem., 39, 142 (1981)) in which lithium carbonate and  $\text{Mn}_2\text{O}_3$  or  $\text{Mn}_3\text{O}_4$  are mixed to a prescribed molar ratio, then heated at 600-650°C to decompose the lithium

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<sup>1</sup> Numbers in the margin indicate pagination in the foreign text.

salt, and further heated at 800-900°C.

[0004] However, when spinel structure  $\text{Li}_x\text{Mn}_2\text{O}_4$  obtained in this manner was used as an active anode substance, there was a problem that the discharge capacity of the obtained lithium secondary battery was small and the cycle characteristic was poor. Manev et al. (J. Power Sources, 41, 305 (1993)) show that when  $\text{Mn}_2\text{O}_3$  is used as a raw material and it is fired at 600°C or higher, the characteristics of the obtained  $\text{Li}_x\text{Mn}_2\text{O}_4$  lithium battery become poor because sintering progresses and a spinel compound having a small relative surface area is produced, and they clarify that electrolytic manganese dioxide or chemically synthesized manganese dioxide is suitable as the raw material. Current methods of producing high-performance  $\text{Li}_x\text{Mn}_2\text{O}_4$  are the following two. One is a synthesis method by Tarascon et al. (J. Electrochem. Soc., 139, 937 (1992)), and in this method, electrolytic manganese dioxide is used for the manganese raw material and lithium carbonate or lithium is used for the lithium salt, and a process of firing at 800°C, gradual cooling and pulverizing is repeated three times, whereby spinel structure  $\text{Li}_x\text{Mn}_2\text{O}_4$  having excellent battery characteristics is produced. However, in this method, not only does it take a long time for manufacturing, but there is a problem that the manufacturing cost also becomes higher. Another method is a synthesis method by

Yoshio et al. (J. Power Sources, 54, 483 (1995)), which is called melt immersion method. In this synthesis method, spinel structure  $\text{Li}_x\text{Mn}_2\text{O}_4$  having excellent battery characteristics can be produced in one firing process using lithium nitrate or lithium hydroxide for the lithium salt. However, lithium nitrate is strongly moisture absorbent and it is difficult to keep the lithium and manganese in a prescribed molar ratio, and not only that, there is also a problem that  $\text{NO}_x$  is produced, being an environmental pollutant which is produced during firing. With lithium hydroxide as well, because it absorbs carbonate gas in the air to produce lithium carbonate, close attention to storage and control of the raw material is necessary and it is not suitable for industrial production.

[0005]

[Problems the Invention Attempts to Solve] The present invention was created in consideration of such problems of the prior art, and its purpose is to provide a method of production of spinel structure  $\text{Li}_x\text{Mn}_2\text{O}_4$  for lithium battery, with which the discharge capacity of a lithium secondary battery having spinel structure  $\text{Li}_x\text{Mn}_2\text{O}_4$  as active anode substance can be greatly increased.

[0006]

[Means for Solving the Problems] The present invention was created in consideration of such problems of the prior art,



and it was achieved by making the particle size of the raw material electrolytic manganese dioxide  $10\mu\text{m}$  or smaller, making the molar ratio of lithium and manganese 0.51-0.53, firing at the melting decomposition temperature of lithium carbonate, then cooling and pulverizing, and further firing at a high temperature of  $700-750^{\circ}\text{C}$ .

[0007] That is, the present invention has aimed to suppress lowering of surface area even if sintering progresses, by selecting manganese dioxide which tends not to undergo progressive sintering, and making the particle size smaller. Because the particle size of the manganese dioxide particles is made  $10\mu\text{m}$  or smaller, the uniformity of distribution during mixture of lithium carbonate and manganese dioxide is markedly increased over the case when ordinary electrolytic manganese dioxide (average particle size about  $40\mu\text{m}$ ) for alkali batteries is used. Therefore, local differences of Li/Mn ratio are eliminated, and production of electrochemically inactive  $\text{Mn}_2\text{O}_3$  and  $\text{Li}_2\text{MnO}_3$  can be prevented. Because local differences of Li/Mn ratio arise and  $\text{Hn}_2\text{O}_3$  <sic> and  $\text{Li}_2\text{MnO}_3$  are produced if electrolytic manganese dioxide having large particle size is used, a spinel structure  $\text{Li}_x\text{Mn}_2\text{O}_4$  having excellent battery characteristics cannot be synthesized without subjecting to a process of pulverizing, mixing and re-firing as in Tarascon et al. Not only do lithium carbonate and manganese

dioxide react at 400°C to produce an oxygen-rich spinel compound, but it takes a long time also for synthesis. Because the lithium carbonate becomes liquid and covers the surface if the synthesis temperature is made greater than or equal to the melt temperature of lithium carbonate (600-650°C), the uniformity of distribution of Li and Mn comes to be further improved than during mixing. The reaction also becomes a solid-liquid reaction, the spinel compound also is produced within 10 hours, and the operability also is improved. The spinel compound produced at this time is a compound being single phase in X-ray analysis (XRD), having a cubic lattice parameter of 8.2Å or less, being oxygen rich, and having a small discharge capacity. Although the production of impure phases in XRD is not acknowledged, because the disappearance of the  $Mn_2O_3$  and  $Li_2MnO_3$  phases is more assured, the intended spinel structure  $Li_xMn_2O_4$  was synthesized by pulverizing and then firing at 700-750°C.

[0008]

[Operation] The reasons why the spinel structure  $Li_xMn_2O_4$  obtained by the

/3

present invention has more prominent effects than the spinel structure  $Li_xMn_2O_4$  synthesized by the conventional method using lithium carbonate are because the particle size of the raw material manganese oxide is small and therefore the

distribution of the lithium carbonate and manganese oxide becomes uniform, and the temperature is raised up to the melt temperature of lithium carbonate so the lithium carbonate melts and reacts with the manganese oxide, and therefore the reaction between the manganese oxide and lithium progresses quickly and uniformly. Therefore, in the synthesis method of the present invention, there is no production the impurities  $\text{Mn}_2\text{O}_3$  and  $\text{Li}_2\text{MnO}_3$ . This is the reason why the discharge capacity becomes greater when it is used as an active anode substance of a lithium secondary battery.

[0009]

[Working Examples] Below, the present invention is explained concretely based on working examples, and the like.

[Working Example 1] 20g electrolytic manganese dioxide and 4.2434g lithium carbonate (Li/Mn ratio: 0.524) were pulverized and mixed and placed in an alumina container. This test material container was placed in an electric oven, the temperature was raised from room temperature to  $600^\circ\text{C}$  in 6 hours, and the temperature was maintained at  $600^\circ\text{C}$  for 10 hours. The temperature was cooled to room temperature in 1 hour, and the test material was extracted. In the XRD chart of this test material, there were no peaks of  $\text{Mn}_2\text{O}_3$  and  $\text{Li}_2\text{MnO}_3$  present, and an analytical peak only of  $\text{Li}_x\text{Mn}_2\text{O}_4$  was

acknowledged. The lattice parameter was computed from the analytical peak to be 8.19Å, and an oxygen-rich spinel compound was produced. When this test material was fired at 750°C for 24 hours in order to reduce the oxygen content, the lattice parameter value was increased to 8.22Å. A lithium secondary battery shown below was constituted using this test material as the active anode substance. For the lithium secondary battery, a rechargeable battery having 18mm inner diameter was used, and the constituting work was performed in a dry box in an argon atmosphere. In Fig. 1, 1 is a cathode terminal, 2 is an insulating material, 3 is a cathode collector plate, 4 is metallic lithium, 5 is a separator, 6 is glass filter paper, 7 is an anode mixture, and 8 is an anode terminal. As the anode mixture, a conductive binder 10mg was added to 25mg of the obtained  $\text{Li}_x\text{Mn}_2\text{O}_4$  and made into a film, and then this was pressed to 18φmm on a stainless steel collector plate. An electrolytic solution having  $\text{LiPF}_6$  (1 mole/l) dissolved in a 1:2 mixed solvent of ethylene carbonate and dimethyl carbonate was used, and charging and discharging were repeated at 1mA current and voltage in a range of 4.5-3.5V. Fig. 2 shows the cycle characteristics of this battery. The discharge capacity at the first cycle is 129mAh/g, and a discharge capacity of 122mAh/g is shown even at the 50th cycle.

[Comparative Example 1] Synthesis was performed under the

same conditions as in Working Example 1 using electrolytic manganese dioxide having an average particle size of about 40 $\mu$ m for the manganese raw material. When XRD measurement of the final product was performed, a  $\text{Mn}_2\text{O}_3$  peak was acknowledged on the low angle side of the (311) area peak. The discharge capacity at the first cycle of this test material is not more than 90mAh/g, and it is as much as 40mAh lower than the working example. When this test material was subjected to a second time of pulverizing and re-firing at 750°C for 24 hours, the  $\text{Mn}_2\text{O}_3$  peak disappeared from the XRD chart. Also, the discharge capacity was increased to 120mAh/g.

[Comparative Example 2] Synthesis of  $\text{Li}_x\text{Mn}_2\text{O}_4$  was performed following the method in Working Example 1 with the molar ratio of lithium and manganese as 0.50 or 0.54.  $\text{Mn}_2\text{O}_3$  was produced as byproduct with 0.50 molar ratio, on the other hand,  $\text{Li}_2\text{MnO}_3$  was produced as byproduct with 0.54 molar ratio. This could be confirmed from XRD. The reason why  $\text{Mn}_2\text{O}_3$  is produced as byproduct with 0.50 molar ratio is probably because the raw material electrolytic manganese dioxide contains 1wt% sulfate radicals. From the fact that single-phase  $\text{Li}_x\text{Mn}_2\text{O}_4$  is produced with 0.51 molar ratio and 0.53 molar ratio, the present synthesis method can be provided with a molar ratio of lithium and manganese in a range of 0.51-0.53.

[0010]

[Working Example 2] 20g electrolytic manganese dioxide and 4.2434g lithium carbonate (Li/Mn ratio: 0.524) were pulverized and mixed and placed in an alumina container. This test material container was placed in an electric oven, the temperature was raised from room temperature to 600°C in 6 hours, and the temperature was maintained at 600°C for 10 hours. The temperature was further raised to 750°C in 1 hour, and firing was performed at 750°C for 24 hours. The product was single-phase  $\text{Li}_x\text{Mn}_2\text{O}_4$ , and the lattice parameter was 8.22Å, being the same value as in Working Example 1. Fig. 3 shows the charge-discharge curve. The shape of the discharge curve was the same as that of the test material in Working Example 1, and the discharge capacity at the first cycle was 124mAh/g, being slightly smaller than that of Working Example 1.

[0011]

[Effect of the Invention] As explained above,  $\text{Li}_x\text{Mn}_2\text{O}_4$  having large discharge capacity and excellent cycle characteristics is obtained by firing 10μm or smaller electrolytic manganese dioxide and lithium at 600-650°C to make an oxygen-rich spinel compound, and then finally firing at 700-750°C.

[Brief Explanation of the Drawings]

[Fig. 1] is a sectional view showing the structure of a

lithium secondary battery pertaining to the present invention.

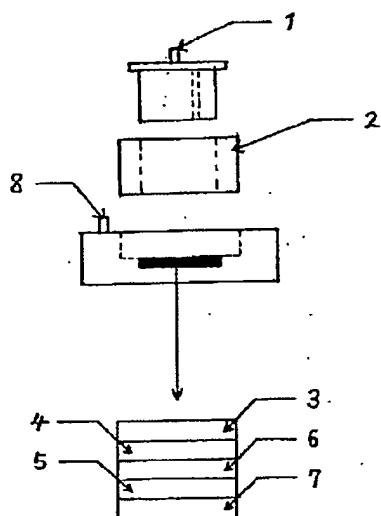
[Fig. 2] is a graph showing the relationship between cycle number and discharge capacity of  $\text{Li}_x\text{Mn}_2\text{O}_4$  obtained by the present invention.

[Fig. 3] is a graph of charging and discharging of  $\text{Li}_x\text{Mn}_2\text{O}_4$  obtained by the present invention.

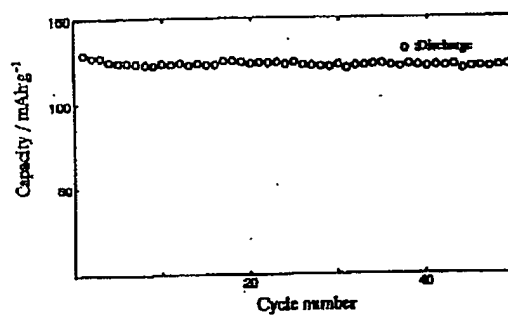
[Explanation of the Symbols]

- 1 Cathode terminal
- 2 Insulating material
- 3 Cathode collector plate
- 4 Metallic lithium
- 5 Separator
- 6 Glass filter paper
- 7 Anode mixture
- 8 Anode terminal
- 9 Charge curve
- 10 Discharge curve

【図1】



【図2】



【図3】

